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Spectroscopic studies of distorted structure bio-nano molecules

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Abstract

In this paper, we have introduced an algebraic technique to Bio Nano-molecules (Porphyrins & Fullerenes) family to determine the Vibrational spectra. An algebraic model of vibrations of polyatomic BioNano-molecules and present, as an example, the vibrational analysis of stretching modes of Nickel Octaethyl Porphyrin (Ni(OEP)), its Isotopomers and bionano molecules. The algebraic technique obtained the results are compared with experimental data; the results are showing good accuracy. Some reassignments of energy levels and predicts location of states not yet observed.

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Keywords: Vibron model, Vibrational Spectra, Energy levels, Porphyrin, Isotopomers, Fullerenes.

1. Introduction

For the last few years, theoretical studies of highly excited vibrational states of polyatomic molecules have been one of the most interesting topics for theoreticians and experimentalists because of the development of new laser spectroscopic techniques. The measurements of highly-excited overtone-combination spectra of molecules have renewed in a theoretical description and understanding of the observed spectral properties. Two approaches have mostly been used so far in an analysis of experimental data: (1) the familiar Dunham like expansion of energy levels in terms of rotations-vibrations quantum numbers and (2) the solution of Schrodinger equation with potentials obtained either by appropriately modifying ab-initio calculations or by more phenomenological methods. In this article, we begin a systematic analysis of overtone-combination spectra and intensities of molecules in terms of novel approach: (3) Vibron model [1-4]. This model is a formulation of the molecular spectral problem in terms of elements of Lie algebra and it contains the same physical information of the Dunham and potential approach.

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However, by making use of the powerful methods of group theory, one is able to obtain the desired results in a much faster and straightforward way. In recent years, these polyatomic bio-molecules (i.e Metalloporphrins) have numerous importance in the field of Chemical Physics. In case of polyatomic bio- molecules the parameters plays major role in the Vibron model. Of course, we have explicitly described with fewer parameters, the vibrational bands of the triatomic linear molecules HCN, OCS [5] and tetratomic molecules HCCF, HCCD by using an algebraic approach [6]. We have also reported the vibrational bands of tetrahedral molecules CCl_4, $SnBr_4$ [7] and polyatomic bio-molecules Nickel Octaethyl porphyrin, Nickel porphyrin molecules using U (2) Vibron model respectively [8]. The advantage of the algebraic approach, as compared to that of Dunham or phonological potential models, is that typically it requires fewer parameters to obtain the same level of accuracy. It also provides a simultaneous description of bending and stretching modes.

We consider in this paper the vibrational modes of polyatomic Bio Molecules i.e Metalloporphrins and its substituted forms. In Sec. 2, we briefly review the theory of Vibron model of vibrations of polyatomic molecules. In Sec. 3, we describe the stretching vibrations of different Metalloporphrins and its substitute forms. Conclusions are presented in Sec. 4.

2. Theory of Lie algebraic Methods

A general algebraic model of rotation- vibration spectra of molecules was introduced in and applied to the study of triatomic and tetra-atomic [9] molecules. In this model rotations and vibrations are treated simultaneously. For this reason, it becomes impractical when the number of atoms exceeds four. However, if rotations and vibrations are separated, it is possible to construct a simpler version of the Vibron model, which can be used for vibrational analysis of large molecules. This model, which we call the one-dimensional Vibron model , starts from the observation that the eigen states of a one-dimensional Schrodinger equation with a Morse potential,

$$h(p, x) = p^2/2\mu + D\,[1-\exp(-\,\alpha\, x)]^2\,, \tag{1}$$

In the algebraic approach, interaction of the type can be taken into account by introducing two terms, called Casimir and Majorana interactions, respectively. If these are added, the total Hamiltonian becomes,

$$H = E_0 + \sum_{i=1}^{n} A_i C_i + \sum_{i\langle j}^{n} A_{ij}\, C_{ij} + \sum_{i\langle j}^{n} \lambda_{ij}\, M\text{-}_{ij} \tag{2}$$

The operators C_{ij} are diagonal, with matrix elements given by

$$\langle\, N_i, v_{i;} N_j, v_j \,|\, C_{ij} \,|\, N_i, v_{i;} N_j, v_j \,\rangle = 4[(v_i + v_j)^2 - (v_i + v_j)(N_i + N_j)] \tag{3}$$

where we have subtracted (relative) the last two terms, since these can be reabsorbed in C_i and C_j. The operators M_{ij} have both diagonal and non-diagonal matrix elements

$$\langle\, N_i, v_{i;} N_j, v_j \,|\, M_{ij} \,|\, N_i, v_i; N_{j,.}\, v_j \rangle = (N_i v_j + N_j v_i - 2 v_i v_j)$$

$$\langle\, N_i, v_i + 1 \,;\, N_j, v_j - 1 \,|\, M_{ij} \,|\, N_i, v_i; N_{j,.}\, v_j \rangle = -\,[v_j(v_i+1)(N_i - v_i)(N_j - v_j + 1)]^{1/2}$$

$$\langle N_i, \nu_i -1; N_j, \nu_j +1 \,|\, M_{ij} \,|\, N_i, \nu_i; N_j, \nu_j \rangle \;=\; - [\, \nu_i(\nu_j+1)(N_j-\nu_j)(N_i-\nu_i+1)]^{1/2} \tag{4}$$

The eigen values of Eq (4) can be easily evaluated and provide a description of n coupled anharmonic vibrators. The couplings in Eq (4) are only first order, in the sense that the operators M_{ij} annihilate one quantum of vibration in bond j and create one in bond i (or vice-verse). In the same way in which one can improve the description of each bond by considering higher powers in the C-operators, one can also improve the description of the couplings by considering higher order terms in the M-operators. We have derived explicit formulas for couplings in which two quanta are annihilated and one is created, for example,

$$\left\langle N_i, \nu_i \pm 2; N_j, \nu_j \mp 1 \middle| M_{ij}^{'} \middle| N_i, \nu_i; N_j, \nu_j \right\rangle \tag{5}$$

and one can generate, in a relatively simple fashion, others, if needed. For applications to the problem described here, these higher order couplings are not needed and we therefore delete them henceforth.

3. Results and discussions

3.1 Sample Vibrational Analysis: Stretching Vibrations of Metalloporphrins and its Isotopomers

As an example of use of the algebraic method we analyze the stretching vibrations of different Metalloporphrins. We number the bonds as shown in figure 1.

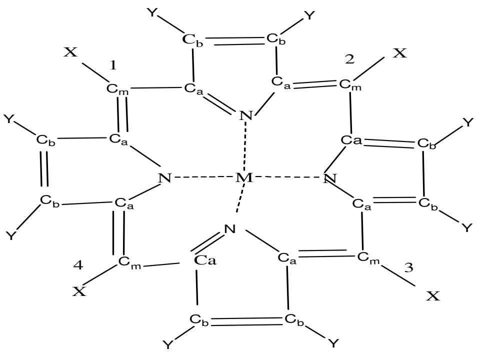

Figure 1.The structure of Metalloporphrins.

Each bond, i, is characterized by its Vibron number N_i, and parameter A_i. The Casimir part of the interbond interactions is characterized by parameter A_{ij}. For the Majorana part we can have, the view of symmetry of the molecule, two possible types of couplings.

One can thus describes all stretching vibrations of **Ni (OEP)-^{15}N, Ni (OEP)-meso-d_4, Ni (OEP)-methylene-d_{16}** in terms of five parameters (N, A, A', λ, λ') as shown in **Table.1**.The Vibron numbers N can be taken from the known anharmonicities of the free C-H or C-C bonds using Eq (3). The data used to determine the parameters are shown in **Table 2**.

Table 1
Comparison between the Observed and Calculated frequencies of the fundamental stretching vibrations

	Ni (OEP)-^{15}N			Ni (OEP)-meso-d_4			Ni (OEP)-methylene-d_{16}		
Sym	$E^{(a)}_{obs}$	E_{Calc}	Δ	$E^{(a)}_{obs}$	E_{Calc}	Δ	$E^{(a)}_{obs}$	E_{Calc}	Δ
C_m-H vibrational mode									
$A_{1g}(\nu_1)$	3041	3041.93	-0.93	2263	2258.49	4.51	3044	3042.03	1.97
$B_{2g}(\nu_{27})$	3041	3040.89	+0.11	2261	2265.38	-4.38	3041	3040.20	0.80
$E_{1u}(\nu_{36})$	3041	3040.01	0.99	2262	2262.30	-0.30	3041	3040.92	0.18
C_b-C_b vibrational mode									
$B_{1g}(\nu_2)$	1604	1604.04	-0.04	1598	1597.05	0.05	1597	1597.35	-0.35
$A_{1g}(\nu_{11})$	1578	1577.96	-0.04	1578	1580.50	-2.50	1567	1568.89	-1.89
$E_{1u}(\nu_{38})$	1588	1590.00	-2.00	1586	1587.97	-1.97	1579	1579.05	-0.05

$^{(a)}$ Observed values taken from the reference [**10**]

Table 2
Values ^{b} of Algebraic Parameters Used in the calculation of C_m –H, C_b-C_b Stretching Modes of Porphyrins and its Isotopomers

	C_m-H vibrational mode			C_b-C_b vibrational mode		
	Ni (OEP)-^{15}N	Ni (OEP)-meso-d_4	Ni (OEP)-methylene-d_{16}	Ni (OEP)-^{15}N	Ni (OEP)-meso-d_4	Ni (OEP)-methylene-d_{16}
N	44	44	44	140	140	140
A	-17.6802	-17.6820	-17.614	-2.83	-2.825	-2.835
A′	-0.24	-0.25	-0.28	-1.223	-1.286	-0.452
λ	0.014	0.01136	0.009	0.086	0.068	0.067
λ	0.011	0.012	0.5685	0.047	0.092	0.020

$^{(b)}$ All values in cm^{-1} except N, which is dimensionless.

We have used in these tables Wilson numbering for the spices of stretching vibrations. It would be very interesting to see whether or not our calculations predict states at the correct. We have explicit calculations up to the fourth overtone (energy up to ≈ 15000 cm^{-1}) as shown in **Table 3 & Table 4.**

Table3.
Comparisons between the experimental and Calculated fundamental vibrational frequencies of C_{60} & C_{70} (Cm^{-1}).

C_{60} molecule

Symmetry	Normal level	$Exp^{(a)}$	Cal	Δ(exp-Calc)
A_{1g}	ν_1	487	485.9303	-1.0697
	ν_2	1473	1472.2039	0.7961

T_{1g}	ν_3	561	562.3943	-1.3943
	ν_4	824	826.3922	-2.3922
	ν_5	1277	1277.2034	-0.2034
T_{2g}	ν_6	555	550.2039	4.7961
	ν_7	723	728.3049	-5.3049
	ν_8	789	788.0293	0.9707
	ν_9	1345	1346.3049	-1.3049
G_{1g}	ν_{10}	480	484.3092	-4.3092
	ν_{11}	565	564.8372	0.1628
	ν_{12}	741	741.2345	-0.2345
	ν_{13}	1073	1076.6573	-3.6573
	ν_{14}	1309	1310.7748	-1.7748
	ν_{15}	1507	1510.6253	-3.6253
H_g	ν_{16}	261	266.3948	-5.3948
	ν_{17}	429	430.8272	-1.8272
	ν_{18}	705	704.2812	0.7188
	ν_{19}	772	776.0893	-4.0893
	ν_{20}	1105	1109.2034	-4.2034
	ν_{21}	1251	1260.6592	-9.6592
	ν_{22}	1426	1427.0983	-1.0983
	ν_{23}	1585	1587.2039	-2.2039
A_u	ν_{24}	947	948.3892	-1.3892
T_{1u}	ν_{25}	527	528.2039	-1.2039
	ν_{26}	577	577.9403	-0.9403
	ν_{27}	1190	1191.2389	-1.2389
	ν_{28}	1431	1432.2930	-1.2930
T_{2u}	ν_{29}	336	339.4857	-3.4857
	ν_{30}	709	708.3849	0.6151
	ν_{31}	958	948.3049	9.6951
	ν_{32}	1177	1182.2784	-5.2784
	ν_{33}	1535	1536.2038	-1.2038
G_u	ν_{34}	351	352.3042	-1.3042
	ν_{35}	737	737.3048	-0.3048
	ν_{36}	751	751.2030	-0.2030
	ν_{37}	1308	1310.2933	-2.2933
	ν_{38}	1435	1438.2039	-3.2039
H_u	ν_{39}	400	399.9483	0.0517
	ν_{40}	530	535.4948	-5.4948
	ν_{41}	666	668.3049	-2.3049
	ν_{42}	728	732.2039	-4.2039
	ν_{43}	1220	1220.2039	-0.2039
	ν_{44}	1434	1437.3948	-3.3948
	ν_{45}	1576	1579.2039	-3.2039

Δ(r.m.s) = 78.0888 cm^{-1}

C_{70} molecules

Symmetry	Normal level	Exp[(a)]	Cal	Δ(exp-Calc)
A'_1	ν_1	428	431.9302	-3.9302

	ν_2	1472	1471.2735	0.7265
A'_2	ν_3	629	630.3940	-1.3940
	ν_4	936	940.3048	-4.3048
	ν_5	1215	1210.2934	4.7066
E'_1	ν_6	533	533.4758	-0.4758
	ν_7	722	723.6785	-1.6785
	ν_8	767	767.0920	-0.0920
	ν_9	1350	1352.7839	-2.7839
E'_2	ν_{10}	479	480.4637	-1.4637
	ν_{11}	675	675.0493	-0.0493
	ν_{12}	735	736.4072	-1.4072
	ν_{13}	1055	1050.8373	4.1627
	ν_{14}	1313	1313.7652	0.7652
	ν_{15}	1516	1514.5869	1.4131
	ν_{16}	245	245.7820	-0.7820
	ν_{17}	408	410.2875	-2.2875
	ν_{18}	714	715.8309	-1.8309
	ν_{19}	1169	1167.0392	1.9608
	ν_{20}	1226	1226.5768	-0.5768
	ν_{21}	1257	1260.6592	-3.6592
	ν_{22}	1433	1429.0983	3.9170
	ν_{23}	1574	1575.2039	-1.2039
A2′′	ν_{24}	892	892.3049	-0.3049
A1′′	ν_{25}	507	504.5068	2.4932
	ν_{26}	573	577.3049	-4.3049
	ν_{27}	1177	1181.6099	-4.6099
	ν_{28}	1432	1432.2930	-0.2930
E''_1	ν_{29}	438	439.3049	-1.3049
	ν_{30}	564	565.4054	-1.4054
	ν_{31}	1143	1145.5748	-2.5748
	ν_{32}	1463	1465.4950	-2.4950
	ν_{33}	318	316.2039	1.7961
	ν_{34}	704	706.9857	-2.9857
	ν_{35}	896	900.6574	-4.6574
	ν_{36}	1206	1210.0398	-6.0398
	ν_{37}	1568	1570.3049	-2.3049
	ν_{38}	1577	1580.7812	-3.7812
E''_2	ν_{39}	304	309.7856	-5.7856
	ν_{40}	701	705.8517	-4.8517
	ν_{41}	920	923.7869	-3.7869
	ν_{42}	1156	1160.6530	-4.6530
	ν_{43}	1517	1520.6652	-3.6652
	ν_{44}	383	384.7854	-1.7854
	ν_{45}	728	728.6755	-0.6755
				Δ(r.m.s) = 68.2436 cm^{-1}

[a] Experimental data has taken from the reference[**20**]

Table 4.

The fitting parameters used in the study of vibrational spectra of fullerene C_{60} & C_{70} is given in Table 2.

	Vibron number	Algebraic parameters		
	N	A	λ	λ′
C_{60}	140	-1.2039	0.0739	-0.4932
C_{70}	140	0.8493	0.0348	0.5903

All values in cm^{-1} except N, which is dimensionless.

We have used the algebraic Hamiltonian to study the highly excited vibrational levels of the molecule **Ni (OEP)-^{15}N, Ni (OEP)-meso-d_4, Ni (OEP)-methylene-d_{16}**. The highly excited vibrational levels, calculated by using the algebraic Hamiltonian Eq. (2), are shown in Figs. 2, 3, 4, 5, 6, & 7.

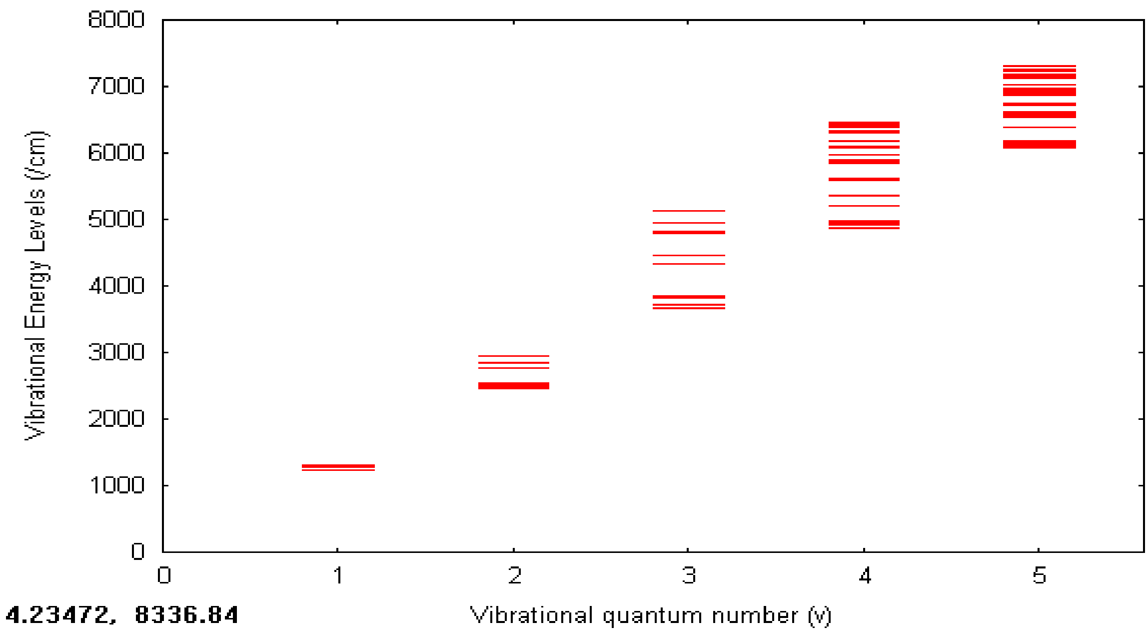

Fig 2. C_m-H band vibrational energy level of **Ni (OEP)-^{15}N**

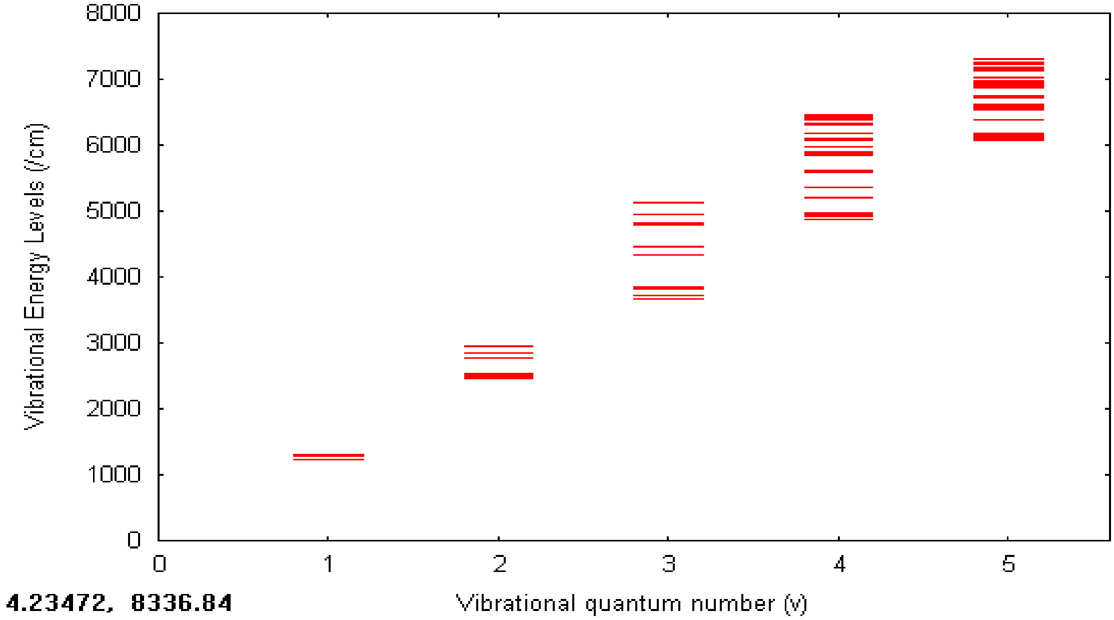

Fig 3. C_m-H band vibrational energy level of **Ni (OEP)-meso-d_4**

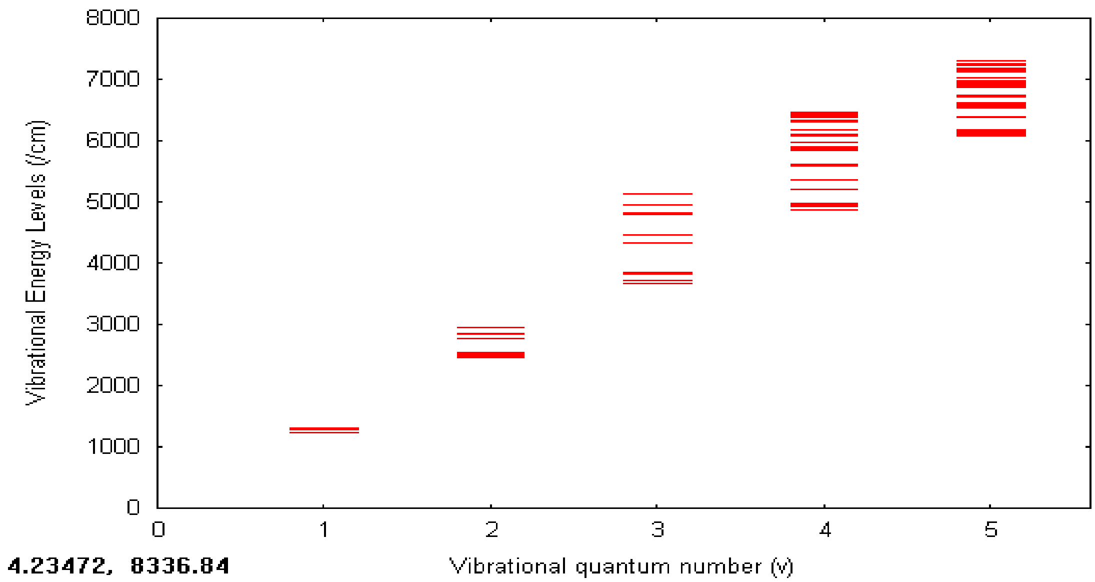

Fig 4. C_m-H band vibrational energy level of **Ni (OEP)-meso-d_4**

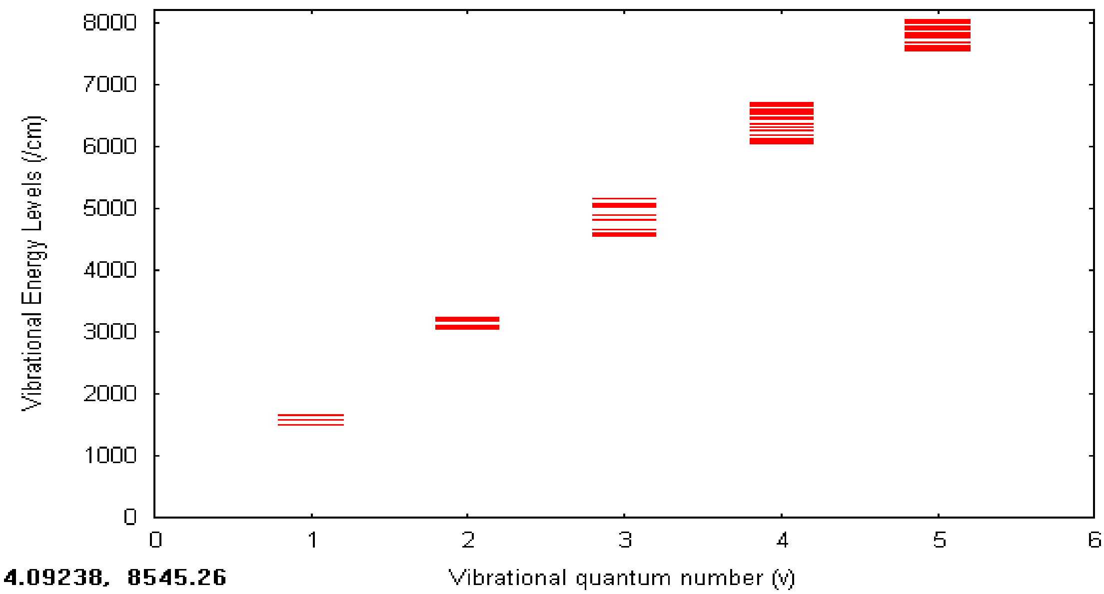

Fig 5. C_m-H band vibrational energy level of **Ni (OEP)-^{15}N**

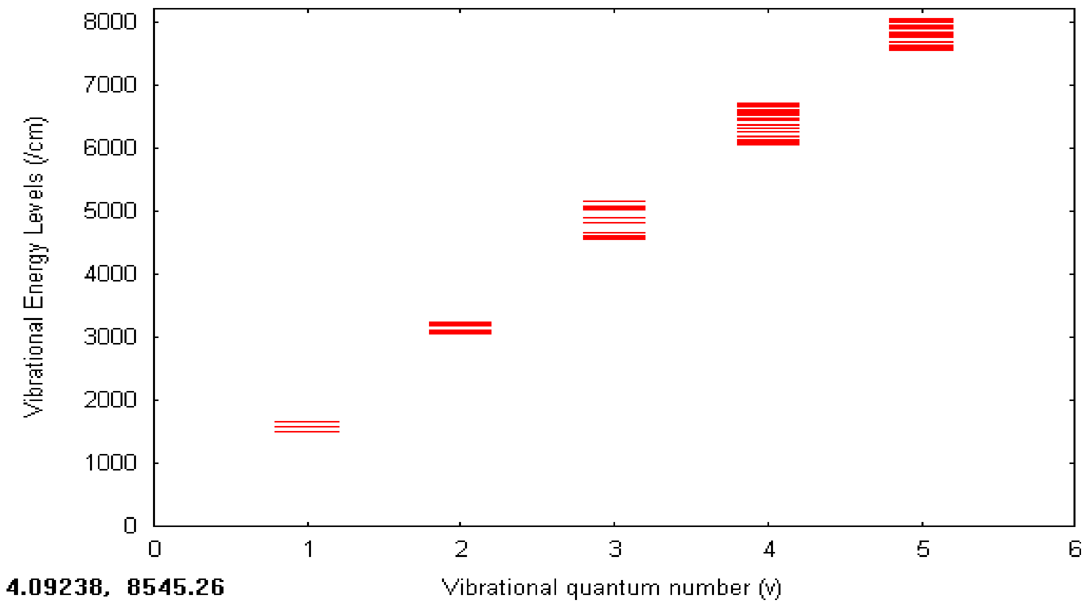

Fig 6. C_m-H band vibrational energy level of **Ni (OEP)-meso-d$_4$**

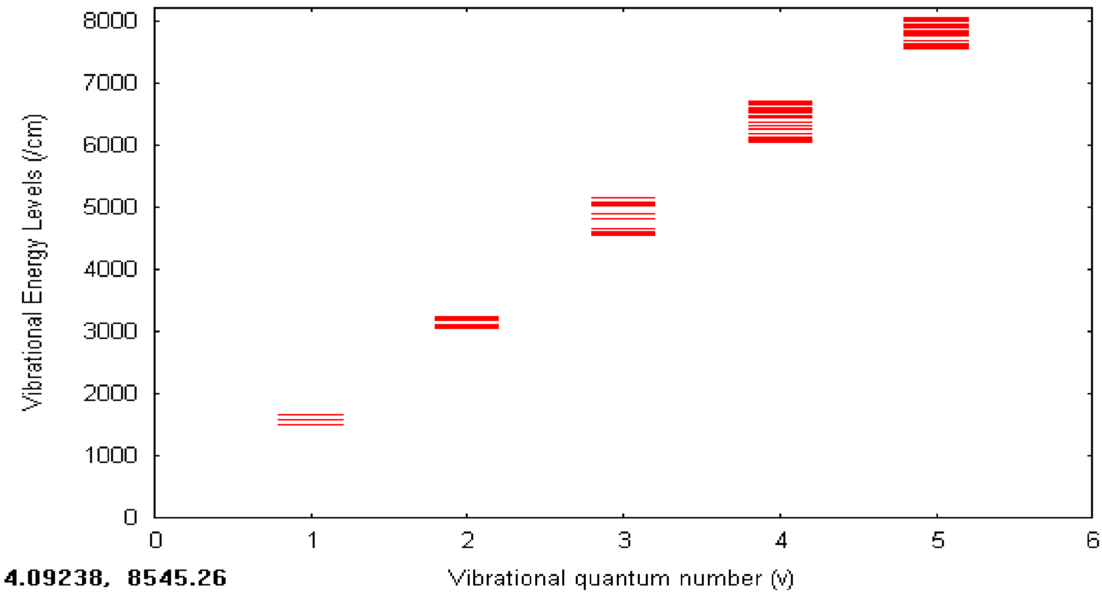

Fig 7. C_m-H band vibrational energy level of **Ni (OEP)-meso-d**

When the quantum number ν increases in a fixed band, the number of energy levels increases rapidly. Usually, the degeneracy or quantidegeneracy of energy levels is called clustering. It may be seen from in Figs. 2, 3,4,5,6 & 7, which the vibrational energy levels of Porphyrins and its Isotopomers make up clusters at excited states.

4. Conclusions

We have presented here a vibrational analysis of the stretching/bending modes of Bio molecules (i.e Nickel Porphyrins) and Nano molecules (Fullerenes C60, C70) in terms of one-dimensional Vibron model i.e U(2) algebraic model. The Nano-molecules C_{60} and C_{70} are I_h and D_{5h} point group symmetry respectively.

In this study the vibrational frequencies of Nano molecules C60 and C70 for 7 vibrational bands, we obtain the RMS deviation i.e Δ(r.m.s) = 78.0888 cm^{-1}, 68.243cm^{-1}, and the locality parameters are ξ_1 = 0.0124, ξ_2= 0.0097 respectively.

Using improved set of algebraic parameters, the RMS deviation we reported in this study for Bio and Nano molecule is lying near about the experimental accuracy. Using only four algebraic parameters, the RMS deviation we reported in this study for Nano molecule are better fit.

The above two points confirm that in four parameters fit, the set of algebraic parameters we reported in this study of local to normal transition provide the best fit to the spectra of Nano molecules.

We hope that this work will be stimulate further research in analysis of vibrational spectra of other Nano molecules like fullerenes and protein molecules where the algebraic approach has not been applied so far. The research work concern is in progress in case of complex Nano systems.

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References

F.Iachello, 1981. Algebraic methods for molecular rotation-vibration spectra, *Chem. Phys. Lett* 78, 581-585.

F.Iachello and R.D. Levine, 1982. Algebraic approach to molecular rotation-vibration spectra. I. Diatomic molecules, *J. Chem. Phys* 77, 3046-3055.

O. S.van Roosmalen, A.E.L. Dieperink, and F.Iachello, 1982. A dynamic algebra for rotation-vibration spectra of complex molecules, *Chem. Phys. Lett*. 85, 32-36.

O. S. van Roosmalen, F. Iachello, R. D. Levine and A. E. L. Dieperink, 1983. Algebraic approach to molecular rotation-vibration spectra. II. Triatomic molecules, *J. Chem. Phys* 79, 2515-2536.

Nirmal Kumar Sarkar, Joydeep Choudhury and Ramendu Bhattacharjee,2006. An algebraic approach to the study of the vibrational spectra of HCN, *Mol. Phys* 104, 3051-3055.

Nirmal Kumar Sarkar, Joydeep Choudhury, Srinivasa Rao Karumuri, and Ramendu Bhattacharjee, 2008. An algebraic approach to the comparative study of the vibrational spectra of *monofluoroacetylene (HCCF) and deuterated acetylene (HCCD), Mol. Phys* 106(5), 693-702.; Nirmal Kumar Sarkar, Joydeep Choudhury and Ramendu Bhattacharjee,2008. Algebraic approach: Study of vibrational spectra of some linear triatomic molecules, *Indian J. Phys* 82(6), 767-772.

Joydeep Choudhury, Srinivasa Rao Karumuri, Nirmal Kumar Sarkar and Ramendu Bhattacharjee, 2*008*. Resonance Raman study on distorted symmetry of porphyrin in nickel octaethyl porphyrin, Pramana J. of Physics 63 (5), 1073-1082.; Joydeep Choudhury, Nirmal Kumar Sarkar and Ramendu Bhattacharjee, 2008. Algebraic approach to analyze the vibrational spectra of tetrahedral molecules,*Indian J. Phys* 82(5), 561-565.

S.R.Karumuri, N.K.Sarkar, J.Choudhury, and R.Bhattacharjee, 2008.Vibrational spectroscopy of Cm-H, Cβ-Cβ stretching vibrations of Nickel metalloporphyrins: An algebraic approach,*Mol. Phys* 106(14), 1733-1738; S.R.Karumuri, J.Choudhury, N.K.Sarkar, and R.Bhattacharjee, 2009. Analysis of Resonance Raman Spectra of Nickeloctaethyl Porphyrin using Lie algebra, *J. Environ. Res & Develop* 3(1), 250-256.; S.R.Karumuri, N.K.Sarkar, J.Choudhury, and R.Bhattacharjee, *Pramana. J. Phys*, 72(3), 517-525 2009; S.R.Karumuri, N.K.Sarkar, J.Choudhury, and R.Bhattacharjee, 2009. Vibrational spectroscopy of CH/CD stretches in propadiene : An algebraic approach, *Chinese Phys.Lett* 26(9), 020308-1-3 *;* S.R.Karumuri, N.K.Sarkar, J.Choudhury, and R.Bhattacharjee, 2009.U (2) algebraic model applied to vibrational spectra of Nickel Metalloporphyrins,*J.Mol. Spectrosc* 255, 183-188 ; S.R.Karumuri, A.S.R.Prasad, 2009. Analysis of Vibrational spectra of Copper Octaethyl Porphyrin [Cu(OEP)] using U(2) algebraic technique, *Int.J.C.M.I* 1(3), 68-72; S.R.Karumuri, J.Choudhury, N.K.Sarkar and R.Bhattacharjee, 2010. Vibrational spectroscopy of Cm–C/Cb–Cb stretching vibrations of copper Tetramesityl porphyrin: An algebraic approach, *Pramana J.Phys.*, 74(1), 57-66

O. S.van Roosmalen, R.D. Levine and A.E.L. Dieperink, 1983.The geometrical-classical limit of algebraic Hamiltonians for molecular vibrational spectra, *Chem. Phys. Lett* 101, 512-517; I. Benjamin, O. S.van Roosmalen, and R.D. Levine, 1984. A model algebraic Hamiltonian for interacting nonequivalent local modes with application to HCCD and H1 2C1 3CD, *J. Chem. Phys* 81, 3352-3352; O. S. van Roosmalen, I. Benjamin, and R. D. Levine, 1984.A unified algebraic model description for interacting vibrational modes in ABA molecules , *J. Chem. Phys* 81, 5986-5998.

Li Xiao-Yuan, Czernuszewicz R S, Kincaid J R, Stein P, Spiro T G, 1990. Consistent Porphyrin Force Field II : Nickel Octaethylporphyrin Skeletal and Substituent Mode Assignments from 15N, meso-d4 and Methylene-d16 Resonance Raman and Infrared Isotope Shifts, *J. Phys. Chem 94,* 47-61. T. Kitagawa, M. Abe, and H. Ogoshi, 1978. Resonance raman spectra of octaethylporphyrinato-Ni(II) and meso-deuterated and 15N substituted derivatives. II. A normal coordinate analysis, *J. Chem. Phys*, 69(10), 4516-4534.; Czernuszewicz R S, Macor K A, Li Xiao-Yuan, Kincaid J R, Spiro T G, 1989. Resonance Raman spectroscopy reveals a1u vs. a2u character and pseudo-Jahn-Teller distortion in radical cations of nickel(II), copper(II), and chloroiron(III) octaethyl- and tetraphenylporphyrins , *J. Am. Chem. Soc* 111, 3860-3869.